STATUS REPORT

ADSORPTION OF A MIXED SURFACTANT SYSTEM ON SILICA

Project BE4A, Milestone 4 FY93 Annual Research Plan

by

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TABLE OF CONTENTS

PAGE

ILLUSTRATIONS

TABLES

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ABSTRACT

Prior work by NIPER on chemical flooding (EOR) enhanced oil recovery processes focused on sulfonate-type surfactants. These surfactants often exhibited limited salinity and temperature tolerance, which in turn affected both the technical and economic success of the method. Mixed surfactant systems for chemical EOR have been studied to broaden the range of temperature and salinity conditions under which chemical flooding can be applied and mobilize residual oil.

When mixtures propagate through porous media, there is a tendency to adsorb and to separate. These processes may lead to the loss of the effectiveness of expensive chemicals. It is therefore important to determine the ability of a mixture to propagate through a porous medium such as a petroleum reservoir.

This status report, as part of Milestone 4 of the BE4A Annual Plan, gives an account of part of an ongoing effort to address the problem of separation of surfactants in a porous medium. This particular work is directed toward learning more about the transmission of surfactant mixtures flowing through a porous material.

A solid with a high surface area was chosen which has different adsorption capacities for anionic and nonionic surfactants so that a good chance of separation might occur. Silica gel with 330 m^2/g was used to make an unconsolidated sandpack. Static adsorption tests were carried out, and a very simple model based on these tests was constructed. The dynamic flow test followed this model in a very general way, but not in detail. The silica did achieve separation of surfactants during the first part of the flow test. The amount of adsorption during dynamic tests was three-quarters of the amount during static tests. Suggestions for future work are given.

INTRODUCTION

Chemical enhanced oil recovery (EOR) processes have the potential for recovering significant amounts of oil. For a number of reservoirs, this may be the only viable method for significantly reducing oil saturation in the field. Surfactants are used to produce the low interfacial tensions (IFT) required for enhanced oil recovery. The IFT of surfactant formulations can be

1

adjusted to the oil by varying the hydrophobe chain length and branching; the required salt tolerance and brine compatibility may be brought about by the addition of an alcohol. However, the alcohol is easily separated from the mixture as it flows through the reservoir. Mixed surfactant systems are of interest because they may not separate as readily as alcohol from the mixture. The primary surfactant could be adjusted to give good IFT and phase behavior, while salt tolerance could be achieved by adjusting the hydrophilic-lipophilic balance (HLB) through the addition of an ethoxylated nonionic surfactant.

Mixed surfactant systems have been shown to have potential for significantly reducing oil saturation in the field. Such mixed systems have been shown to have potential advantage over conventional chemical flooding systems because they show improved tolerance and adaptability to different reservoir conditions of salinity and temperature while maintaining the ability to mobilize residual oil. Puerto and Reed[1] consider mixed surfactants to be necessary to adjust the optimum conditions to fit those of the reservoir. Maini and Batycki[2] have reported on the synergistic effects of mixed surfactant systems.

NIPER is currently working on the synergistic effects of the combination surfactants of different type and structure on the overall tailoring of the system to different reservoir conditions.[3,4,5] Screening of mixed surfactant systems included mixtures of commercial sulfonated surfactants as primary components and ethoxylated anionic or nonionic surfactants as secondary components. Evaluation of these systems included measurements of physical properties, IFT measurements, phase behavior, phase inversion temperature and oil displacement measurements.

When a surfactant slug is propagated through a porous medium such as a reservoir, there is the possibility of adsorption, precipitation, or chromatographic separation of components. Adsorption and precipitation lead to loss of valuable chemicals, while chromatographic separation even without serious loss of material can lead to component separation and loss of effectiveness. The amount of adsorption and separation of surfactant components that occurs during chemical flooding is important for both technical and economic reasons.

During the adsorption of mixed surfactant systems, the presence of one surfactant type influences the adsorption of the other type. Somasundaran and coworkers[6] have found the following results for adsorption of an anionic-nonionic mixture on silica: (1) The adsorption of sodium dodecylsulfate (anionic) is very low; (2) The adsorption of octylbenzene ethoxyalate (nonionic) is moderate; (3) The presence of the anionic increases the adsorption of the nonionic in the premicellar region, while the maximum adsorption (plateau) is little affected; and (4) The

adsorption of anionic is greatly increased by presence of the nonionic. The point of zero charge of a mineral is the pH at which the net surface charge vanishes. This point is pH 2 for silica;[7] it is positively charged at lower pH and negatively charged at higher pH. The reason for low adsorption of anionic surfactants on silica is that under typical oilfield pH values, the negative charge on the silica has an electrostatic repulsion for the negatively charged surfactant anion. However, nonionic surfactant does adsorb because of the absence of this electrostatic repulsion. Once the nonionic surfactant has adsorbed on silica, the anionic surfactant adsorbs by chain-chain interaction.

On kaolinite, Somasundaran et al.[8] found that both the nonionic and anionic adsorb, and the presence of one surfactant type increases the adsorption of the other, especially in the premicellar region. At neutral pH values, the kaolinite has regions of positive and negative charge,[8] and the anionic surfactant ions are attracted to the positive areas. For mixed surfactants, each type can adsorb on the other by chain-chain interactions. Harwell and Scamehorn[9] indicate that the adsorption characteristics of a surfactant can be varied by mixing surfactant types.

Task 4 of BE4A examines the ability of surfactant formulations to propagate through reservoir material without losing their effectiveness, either from excessive loss or from excessive change of the mass ratio of one surfactant to another. The ability of a system to propagate through porous media will need to be a part of the investigation of suitable surfactant formulations. During FY93, it was the immediate objective of this task to analyze an anionic and a nonionic surfactant singly and in their mixture, to perform static (bottle) tests of adsorption of each surfactant and of the mixture, to make a simple model of the expected adsorption behavior, and to run a dynamic test of adsorption. In this flow test, the breakthrough behavior of the mixed surfactant system was determined. This mode of proceeding is similar to that in frontal analysis chromatography.[10-17]

EXPERIMENTAL

The surfactants selected were commercial surfactants currently available and which have been previously used in this project. Therefore, Stepan B-100, an alkyl aryl sulfonate was selected, along with Igepal DM-530, a dinonylphenoxy ethoxylate. All solutions were prepared as w/w percent. A moderate salinity brine of 1% NaCl was selected. The anionic surfactant does not separate or precipitate in this brine. Solutions of each individual surfactant were prepared containing 1% active weight of surfactant in 1% NaCl. A mixture was also prepared containing 1% of each surfactant in 1% NaCl. No low-molecular-weight alcohol was added to any of the solutions.

3

Silica gel was selected as the model reservoir material for this initial investigation. The pH of the surfactant mixture was 8.6, which ensured that the silica would retain its negative surface charge. No clays or oil were present. Davison™ grade 62 (D62) silica gel was used as the adsorbent. This silica gel has a very high specific surface area of 330 m^2/g, but it is not a microporous material. Reservoir material generally has a specific surface of 1 to 2 m^2/g, and the clay content is responsible for most of that surface area. An unconsolidated sandpack of silica gel 1 foot long can represent the silica content of a few hundred feet in the reservoir. Another reason for selecting the high surface area material is to provide a test in which the surfactants have a good chance of separating in a laboratory-scale apparatus. The silica was screened, and the portion which was 60-100 mesh (over 90% of the original material) was used. The silica was heated to 300° C overnight and cooled in a desiccator over Drierite™ before use.

Ionic surfactant was analyzed using a well-known two-phase titration method.[18,19,20] This method is a two-phase, dye-transfer titration using hexadecyltrimethyl ammonium bromide as titrant and methylene blue as indicator. The sample, an aqueous solution of indicator, and chloroform were added to a stoppered volumetric flask and shaken. In the presence of sulfonate, the bottom layer is highly colored. The titrant is added until both layers have the same color intensity. Sample sizes were scaled so that less than 2 milliliters of titrant was used. Stock solution of the mixed surfactants was used to standardize the titration. The nonionic surfactant does not interfere with this procedure.

The method of Boyer et al.[21] was selected to determine the concentration of the nonionic surfactant. This method consists of the separation of the nonionic from the anionic surfactant and the colorimetric determination of the nonionic surfactant. A 1-mL sample is washed through an anion-exchange column of BioRad™ AG™ 1-X to retain the anionic surfactant while the nonionic surfactant is eluted with methanol. The methanol is removed on a rotary evaporator, and the dried nonionic surfactant is taken up in methylene chloride. Aqueous cobalt thiocyanate solution is added, shaken and the organic layer separated. The optical absorbance of the organic layer is measured at 620 nm.

Calibration of the nonionic analysis was carried out using the mixed surfactant solution containing 1% of each the anionic and the nonionic surfactants as the stock solution. Solutions containing 0.20, 0.40, 0.60, and 0.80% surfactant were made by adding 1% brine to the stock solution. The results of this standardization is shown in Fig. 1. The points are the measured absorbance vs. concentration, while the line is the quadratic least-squares fit to the points.

For static adsorption determination, various measured amounts of silica were added to various amounts of solution in capped tubes. These tubes were agitated for at least 24 hours and then allowed to settle. Aliquots were removed and analyzed for surfactant concentration.

The unconsolidated sandpack was prepared in the following manner. 25 cm of 3/8-in. thin wall stainless steel tubing was fitted at each end with a 3/8 to 1/8 in. reducer. Glass wool was packed in each 3/8-in. reducer to support a 400-mesh screen. 5.1861 g silica was packed into the tube with frequent tapping. Inlet and outlet valves were fitted on the tube. The sandpack was evacuated with a vacuum pump; carbon dioxide was admitted to the sandpack and it was evacuated again. The carbon dioxide flush was performed twice, then the sandpack was evacuated and saturated with deaerated 1% NaCl brine. The pore volume of the sandpack was 11.4 mL, and the porosity was 81%.

The dead volume of the tubes, valves, and fittings, determined by weighing before and after filling with water, was 3.5 mL. The effluent volume was corrected by subtracting the dead volume from the produced volume.

After saturation, the pack was equilibrated overnight with a flow of 6 mL/hr of brine solution. Mixed surfactant solution was admitted to the sandpack at this same flow rate and collected in nominal 2.5-mL aliquots. After 163 mL had been collected, the flow rate was adjusted to 2.5 mL/hr, and the experiment was left over a long weekend. A total of 572.5 mL of effluent
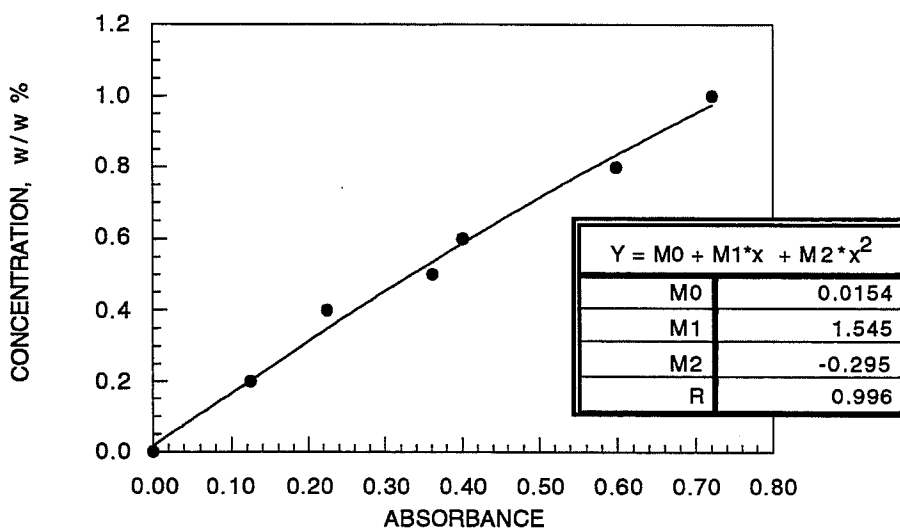

$Y = M0 + M1*x + M2*x^2$	
M0	0.0154
M1	1.545
M2	-0.295
R	0.996

Figure 1. Standardization of the nonionic surfactant analysis.

was collected.

RESULTS

Static Adsorption Tests

The results of the static adsorption of surfactants above the critical micelle concentration (CMC) are presented in Table 1.

The CMCs of these anionic, nonionic and mixed surfactants are much lower than 1%; therefore, these adsorption quantities are maximum or plateau adsorptions; these measurements do not and were not intended to provide a complete adsorption isotherm. By itself, the nonionic surfactant has an adsorption on silica gel of 740 mg/g or 2.4 mg/m^2, while in the presence of the anionic, its adsorption is 588 mg/g or 1.8 mg/m^2. In the absence of nonionic, the anionic surfactant has an adsorption of 26 mg/g (0.08 mg/m^2), while in the presence of the nonionic, the anionic surfactant adsorbs to the extent of 373 mg/g (1.1 mg/m^2). For a typical sandstone material with a specific surface area of 1 m^2/g, the adsorption in mg/g is numerically the same as adsorptions given above in terms of mg/m^2. Each surfactant has an effect on the adsorption of the other. The anionic causes a lowering of the nonionic adsorption, perhaps because it incorporates charges into the adsorption layer; while the presence of adsorbed nonionic surfactant greatly increases the adsorption of the anionic, probably because the anionic surfactant interacts with the adsorbed nonionic surfactant by chain-chain interactions.

A very simple model of these results was constructed. This model does not contain dispersion or an isotherm for adsorption below the CMC. It models the adsorption as follows:
1. The nonionic surfactant will always have anionic surfactant with it; in the presence of the anionic surfactant, the maximum adsorption of the nonionic surfactant is 550 mg/g.
2. In the absence of nonionic surfactant, the anionic adsorbs to a maximum of 25 mg/g.

TABLE 1. - Results of static adsorption tests

Anionic adsorption		Nonionic adsorption	
mg/g	mg/m^2	mg/g	mg/m^2
Single surfactant adsorption tests			
26 ± 5	0.079 ± 0.015	740 ± 131	2.42 ± 0.40
Mixed surfactant adsorption test			
373 ± 84	1.13 ± 0.25	588 ± 145	1.78 ± 0.44

3. In the presence of nonionic surfactant, the maximum anionic adsorption is 25 mg/g plus 0.65 times the anionic adsorption amount.
4. The adsorption of the tracer is 0.
5. The input concentration of both surfactants as well as that of the tracer is 1%, or 10 mg/mL of solution.

The model has five cells, each containing 1 gram of silica and 2.24 g of solution. The model has the same PV as the sandpack. Solution is equilibrated with the solid in cell one; the contents of this first cell are moved to the second cell, and fresh solution moved into the first cell. This process is repeated until about 500 mL of effluent has been recovered from the model.

The results of this model calculation are presented in Fig. 2 in terms of mL of effluent. Data from corefloods an often presented in terms of pore volumes (PV) of fluid. Since the solid in the unconsolidated sandpack has such a high specific area, presenting the data in terms of PV of the core is misleading. For example, a typical core (such as Berea sandstone) with the same surface area as the unconsolidated silica (1,712 m^2), having a specific surface area of 1 m^2/g, a density of 2.1 g/mL and a porosity of 22% would have a PV of 151 mL. This quantity will be referred to later as the "equivalent pore volume."

Figure 2 shows the results of modeling the flow of surfactant through 5 g of silica. The tracer breaks through after 11.4 mL, which is 1 PV. The anionic breaks through at an intermediate concentration after 40 mL, and both anionic and nonionic come through at full strength after 280 mL. Because of the high surface area of this material, 300 mL amounts to 2 equivalent pore volumes of material with a surface area more representative of reservoir rock.

Dynamic Adsorption Tests

The results of the dynamic adsorption test are shown in Table 2 and are presented in Fig. 3. The last column of Table 2 indicates the ratio of anionic to nonionic surfactant in the effluent fluid. Since the input fluid had a 1:1 ratio, this column indicates the effect of different adsorption characteristics of surfactants, which is also visible in Fig. 3 as the separation between the curves. At least some nonionic surfactant accompanies most of the anionic surfactant through the porous medium, and separation of the components as observed in the simple model does not occur. Surfactant breakthrough was evident to visual inspection at 15.3 mL, or just over 1 PV of the unconsolidated sandpack. The analysis showed that the first anionic surfactant came through at low concentration at about 1 PV.
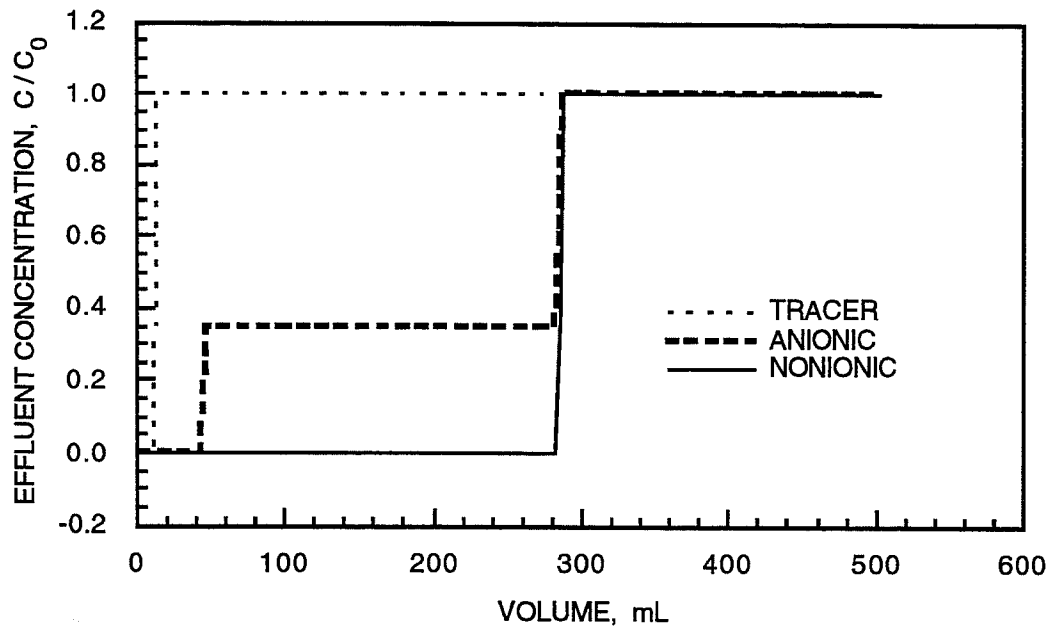
7

FIGURE 2. - Chemical breakthrough for model sandpack flood.

There are some similarities as well as striking differences between Figs. 2 and 3. Both figures show the separation of surfactants occurring, with the anionic surfactant running ahead of the nonionic. They agree that during the separation phase, the difference between the concentrations of the surfactants as shown by the vertical separation of the curves is about the same, namely about 0.35 C/C_0 units. The 1:1 ratio of surfactants appears at about 280 mL in each figure (just less than 2 equivalent PV).

It is interesting to note that in Fig. 3, there is no visible effect on the curve because of the change in flow rate which occurred at 163 mL. The spike on the curve occurred at 67 mL and probably represents a slight adjustment of flow paths through the bed, since it affected both anionic and nonionic effluent concentrations. On the other hand, the square corners of Fig. 2 have been rounded off in Fig. 3. This is not surprising, since the very simple model contains no provision for dispersion of the fluid as it moves through the sandpack. Also the assumption of instantaneous adsorption is an oversimplification.

8

TABLE 2. - Results of dynamic adsorption test

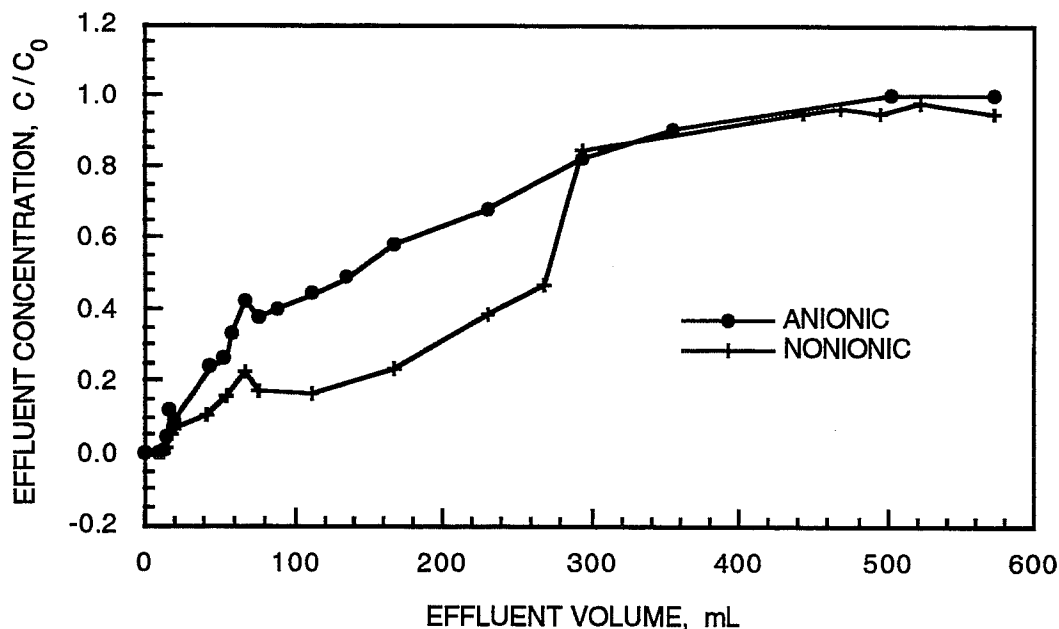| Effluent volume, mL	Anionic surfactant concentration, C/C_0	Nonionic surfactant concentration, C/C_0	Anionic/nonionic, ratio
10.2	0	0	
12.7	0.006	0	
15.3	0.044	0.015	2.93
17.8	0.116	0.054	2.15
20.3	0.090	0.068	1.32
42.0		0.106	
44.2	0.239		
53.2	0.258	0.158	1.63
57.9	0.332		
67.0	0.423	0.225	1.88
76.2	0.376	0.177	2.12
88.2	0.398		
111.6	0.440	0.162	2.72
135.6	0.484		
168.1	0.581	0.233	2.49
230.7	0.677	0.384	1.76
268.8		0.465	
293.4	0.823	0.844	0.98
354.8	0.903		
442.4		0.95	
469.0		0.964	
495.4		0.948	
503.3	1.00		
522.3		0.979	
572.5	1.00	0.95	1.05

9

FIGURE 3. Chemical breakthrough for the dynamic adsorption test.

Of more significance is that the surfactants break through much sooner than the model predicts. At least some of both surfactants moved through the silica gel, although in approximately a 2 / 1 ratio of anionic / nonionic. Thus the surfactants penetrated further through the porous medium than predicted by the model. There are several reasons for this difference. The model is based on an over-simplified adsorption isotherm, which assumes that the surface will strip all surfactant from a stream of low-concentration fluid until its adsorption capacity is reached, and then stop adsorbing. However, in the dynamic situation, the surfactant concentration is lowered, but not reduced to zero. During flow through the unconsolidated particles, part of the fluid in contact with the particle moves very slowly, and adsorption occurs through this semi-stagnant layer. Thus fluid moves forward before complete adsorption equilibrium is established. Another process occurring is that the adsorption of one surfactant may influence the behavior of the other in ways that alter the dynamics of the process. In the dynamic test, the silica which is closer to the exit is bathed with fluid much depleted in nonionic surfactant so that some anionic surfactant adsorbs on the silica surface. This anionic surfactant interferes with the ability of the nonionic surfactant to adsorb when it comes later.

In Fig. 3, the area under each curve represents the amount of each surfactant which appears in the effluent fluid. The area above the curve and below the line marking a relative concentrion of one (C/C$_0$) represent the quantity of surfactant that is missing, i.e. that is still in the sandpack. Of

10

the surfactant remaining in the sandpack, the quantity held by 1 PV (11.4 mL) of fluid is corrected; the surfactant in this fluid is not adsorbed by the solid. The adsorption of anionic surfactant is displayed in Table 3. Even though a large amount of fluid has passed through the sandpack, the adsorption of each surfactant is about 75% of the amount predicted by the static tests.

TABLE 3. - Surfactant adsorption during dynamic flow test

	Dynamic adsorption, mg/g	Dynamic adsorption, mg / m²	Static adsorption, mg / m²	Dynamic/ static, ratio
Anionic	295	0.89	1.13	0.79
Nonionic	435	1.32	1.78	0.74

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The ability to propagate mixed surfactant systems through the reservoir is important for successful application of chemical EOR technology. In this investigation, the general features of a simple model for the propagation of mixed surfactant systems were found in the dynamic flow test. The surfactant mixture traveled through the sandpack in a different ratio than the injected ratio until the adsorption requirements were satisfied.

For future work, tests should be run on the behavior of surfactant slugs as opposed to continuous injection. A useful variation may be a test in which a slug is followed by polymer to see if the presence of polymer might have an influence on maintaining the integrity of the surfactant slug. A more realistic test will require the use of a surfactant system optimized for a particular salinity, temperature and oil; clay along with silica in the sandpack; and the presence of oil; and running tests for oilfield conditions. Perhaps the most satisfactory information might be obtained by running a coreflood with a good polymer system, measure the recovery of oil, and analyze the amount of anionic and nonionic surfactant in the effluent brine, effluent oil, and the amount retained by the core. Also adsorption experiments using an HLB gradient may be run. Development of rapid analytical techniques for the specific surfactants present in a promising surfactant mixtures is of high priority so that the required information may be obtained with much less time and effort.

The use of sacrificial agents may be helpful. Even an agent which has small effect on the anionic surfactant alone may be very useful if it prevents the nonionic from adsorbing, for this will decrease both the total adsorption and keep the surfactant mixture within its design specifications.

Usually the nonionic surfactant is used to increase the salinity tolerance of the anionic surfactant. If the anionic surfactant precipitates when separated from the nonionic surfactant, this might constitute a system which will be self-sharpening, since much of the anionic surfactant which advances ahead of the mixture will be immobilized until the main slug catches up with it.

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